POTENTIAL DISTRIBUTION IN LIQUID FLOW-THROUGH POROUS CARBON ELECTRODES

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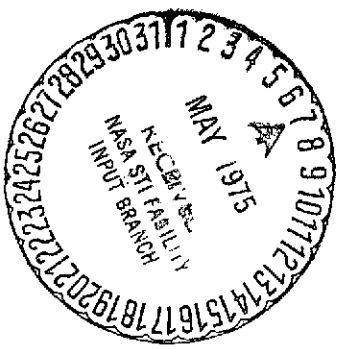

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16. Abstract

The potential distribution in liquid flow-through porous carbon electrodes as a function of the cathode reactions of dissolved oxygen and hydrogen peroxide was investigated. The potential distribution depends on the electrolyte flow rate, its flow direction and the current density. The theoretical and experimental correlation of total current and frontal polarization of the porous electrode was shown. And the advantages in using a thin electrode with hydrogen peroxide and in applying electrolyte flow from the front of the electrode were discussed.

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POTENTIAL DISTRIBUTION IN LIQUID FLOW-THROUGH POROUS CARBON ELECTRODES

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1. Introduction

There have been numerous theoretical findings on the current and potential distribution in porous electrodes. Experimentally, however, only the potential distribution measurements within a dry cell where the resistance of the electrode is relatively high have been obtained by Coleman [1] and Fukuda and Hirai [2]. When liquid flow-through porous electrode (either carbon or porous metal) is used, one can ignore the negligible amount of resistance in the electrolyte fluid and of the electrode. Therefore, the liquid flow-through porous electrode is ideal for the analysis of the reaction distribution within an electrode. Hence, a study of various factors influencing the reaction distribution of liquid flow-through carbon electrodes was started. The measurements of cathode reaction with dissolved oxygen and hydrogen peroxide were used due to the familiarity of the technique. The relations between the change in potential distribution and flow rate, flow direction, current density, dissolved oxygen and hydrogen peroxide concentration distribution were studied. From these results the relation between the thickness of the electrode and potential distribution was investigated.

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2. Experimental

The measurement of potential distribution of cathode reaction was taken at a constant current, as various concentrations of oxygen or hydrogen peroxide in one normal potassium hydroxide solution were added to the electrode. The porous carbon electrode (carbon filter: porosity = 50%, average opening = 20μφ45μφ,

*Numbers in margins indicate pagination in the foreign text.

thickness = 1.5-4.5 mm) contained prescribed amounts of silver or platinum as a catalyst. To this electrode Luggin capillaries (0.5-0.7 mm$^{\phi}$) were inserted (Fig. 1) at various depths, and secured by epoxy resin (care was taken to avoid plugging of porous surfaces). These capillaries were connected to the reference electrode (mercury) with a silicon rubber tube. Filter paper was used to plug the capillary to avoid bubbles and leakage.

The potential readings within the electrode were taken after the potential stability was reached at the forward end of the electrode and recorded only if it was stable during and immediately after the readings. Also, to avoid errors due to the fineness of the capillaries and the long flow distance between the experimental electrode and the reference electrode, an impedance converter was placed between the electrodes and the recorder. The flow rate and flow direction (from the front side or the back side of the electrode) were also measured. /232

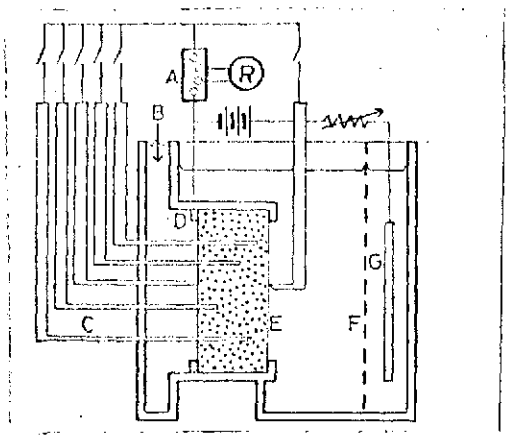

Fig. 1. Schematic diagram of the experimental apparatus

Key:
A. Impedance converter
B. Inlet of electrolyte
C. Luggin capillary with reference electrode
D. Current collector (Ni ring)
E. Porous carbon electrode
F. Diaphragm
G. Counter electrode
R. Recorder

3. Results and Discussion

3.1. Cathode reaction of dissolved oxygen

It is thought that the reaction distribution current, potential, and concentration) within a porous electrode is not constant due to the resistance or reactions from the electrode and/or

electrolyte. So, the potential measurements were made at the front and the back side of the electrode simultaneously. The result is plotted as the polarization curve in Fig. 2. The large difference shown tends to be larger if the current density is higher. This polarization curve is very similar to the one obtained by Perskaya [4] and Austin [5]. Then, the thickness of the electrode was varied and the potential differences between the front and back side of the electrode were measured. As the electrode becomes thicker, the potential difference becomes larger (Fig. 3.). The amount of catalyst added was proportional to the weight of the carbon electrode.

From Fig. 2 and 3 the nonuniformity of the potential distribution can only be assumed. So, the potential distributions with varied current densities were measured (Fig. 4). Here, the horizontal scale indicates the ratio of electrode thickness. This graph shows a smooth and proportional relation between the current density and the potential distribution. We can assume the change in concentration of dissolved oxygen in the electrode when the flow rate changes. Then, the potential distribution with different flow directions was studied. When the flow rate is high and the current density low, the potential distributions of the different flow directions are parallel (Fig. 5). But when the current density is high and the flow rate low, the polarization on the back side of the electrode with the flow from the front of the electrode is larger than that with the flow from the back. And the converse is true for the polarization distribution /233 to be higher on the front side of the electrode [6]. Therefore, when the flow is applied from the back side, the

polarization on the front side becomes more dense and when the flow is applied from the front side, the polarization on the front side becomes less (Fig. 6).

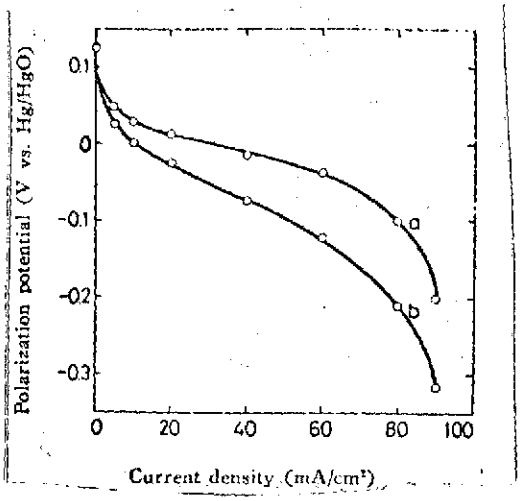

Fig. 2. Polarization curves of back side and front side of electrode

C/Pt (20μφ), 3.0 mm thick, 50 cc/min/cm^2

Key: a. Rear side potential
b. Front side potential

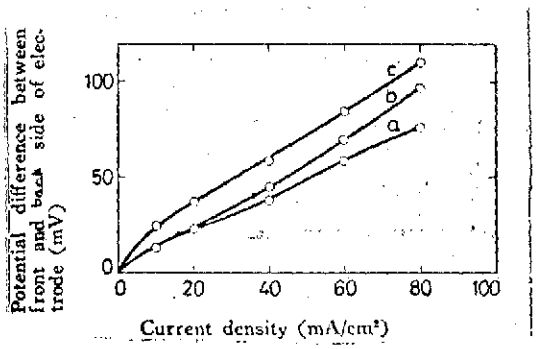

Fig. 3. Effects of electrode thickness on the difference of polarization potential between front and back side of electrodes

C/Pt (20μφ), 50 cc/min/cm^2
Electrode thickness (mm)
a: 1.4; b: 2.0; c: 3.0.

3.2. Cathode reaction of hydrogen peroxide

Since the reactivity of hydrogen peroxide is high among many cathode reaction materials and its handling is easy, the effects of varying concentrations of hydrogen peroxide on the potential distribution were studied along with varying electrolyte (hydrogen peroxide) flow rate and current density.

The effect of varying electrolyte flow rate on the potential distribution is shown in Fig. 7. When the flow is increased, the polarization potential decreases, and the potential distribution tends to average out. At high current density, uneven potential distribution was observed as the flow rate became low. This unevenness was thought to be due to the concentration distribution of hydrogen peroxide. So when the potential distribution

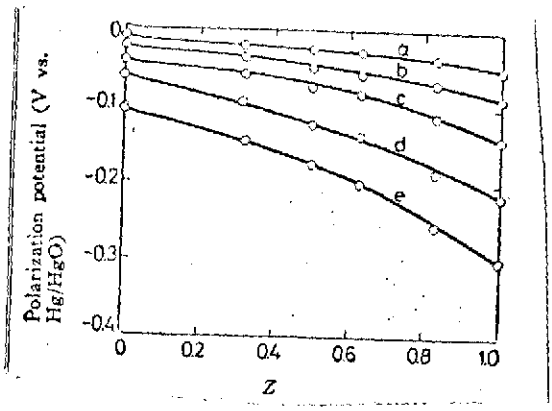

Fig. 4. Potential distribution curves

C/Pt (20μ$^{\phi}$), 3.0 mm thick, 50 cc/min/cm^2

Current density (mA/cm^2)

a: 20; b: 40; c: 60; d: 80; e: 100.

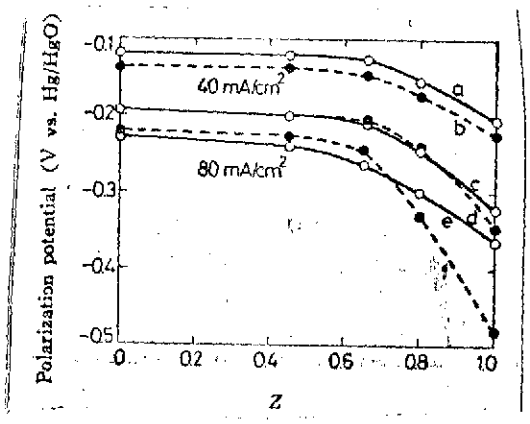

Fig. 5. Potential distribution curves

C/Ag (20μ$^{\phi}$)

Flow rate (cc/min/cm^2)

a,b,c,d: 100; e,f: 50

Solid line: Electrolyte flow through from front side of electrode

Dashed line: From rear side

was investigated at different concentrations of hydrogen peroxide, it was discovered that as the concentration became lower, the unevenness started to appear. Moreover, when current density is very high and flow rate is very low, the uneveness appeared. Therefore, these /234 phenomena are due to the concentration polarization, but such an observation did not take place with dissolved oxygen. That is, approximately 65% of the hydrogen peroxide goes through electrolytic decomposition at the flow rate of 5.00 cc/min/cm^2 within the electrode. This reaction is the logarithmic relation to the thickness of the electrode. Generally, the potential distribution of a porous electrode is determined by the nature of the electrochemical reaction and the resistance of the electrode and the electrolyte with the cathode reaction of the dissolved oxygen. The electrochemical reaction affects the concentration distribution within the electrode. The electrolytic effect of hydrogen peroxide is so large that the concentration distribution in the electrode is affected by

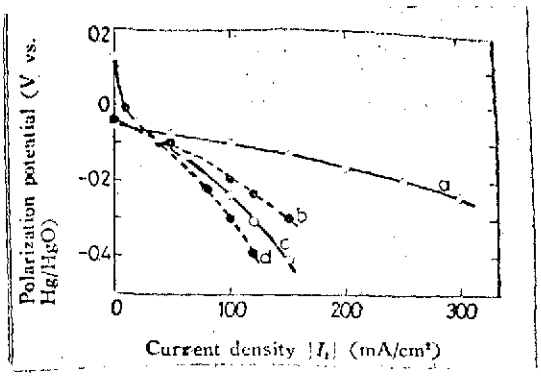

Fig. 6. Polarization curves

C/Pt (20μϕ), 3.0 mm thick

a, b: 0.1N-H_2O_2, 5.0 cc/min/cm^2; c,d: Dissolved oxygen, 80 cc/min/cm^2

Solid line: Electrolyte flow-through from front side of electrode.

Dashed line: From rear side.

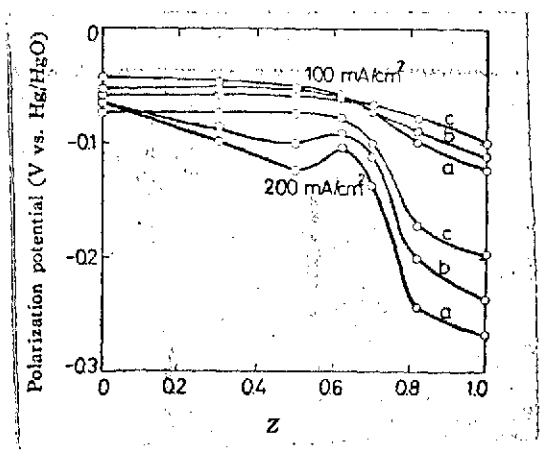

Fig. 7. Potential distribution curves

C/Pt (20μϕ), 3.0 mm thick, 0.05 N-H_2O_2

Flow rate (cc/min/cm^2)

a: 2.0; b: 5.0; c: 10.0

both decomposition materials and the electrochemical reactions proper. This explains the unevenness of the potential distribution. That is, since the potential distribution is higher toward the front part of the electrode, the current distribution is also higher in that part. When the unevenness is observed, the change in concentration distribution becomes larger than that in current distribution. This observation correlates very well with the theoretical calculation of the potential distribution and calculated unevenness reported by Bagotskii, et al [7].

From the results so far, we have found that potential distribution is higher at the front part of the electrode. Now, we have varied the thickness of the electrode and investigated their effects. Fig. 8 shows the potential difference between the front and back side of the electrode as a function of the thickness of the electrode when the current density was changed. The polarization potential does

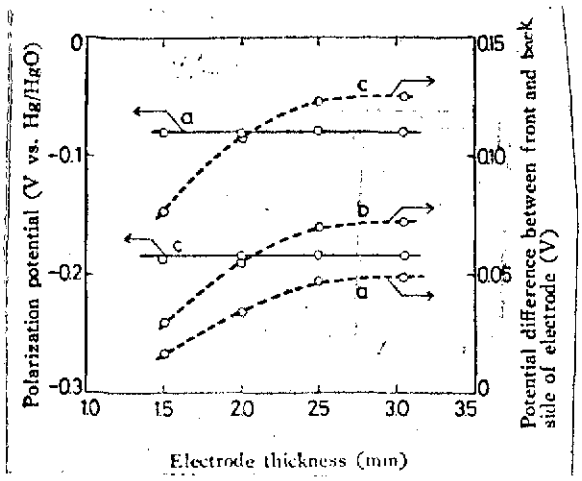

Fig. 8. Effects of electrode thickness on polarization potential at front side of electrode and the difference of polarization potential between front and back side of electrodes.
C/Pt (20μ$^{\phi}$), 0.05 N-H_2O_2, 5.0 cc/min/cm^2
Current density (mA/cm^2)
a: 100; b: 150; c: 200

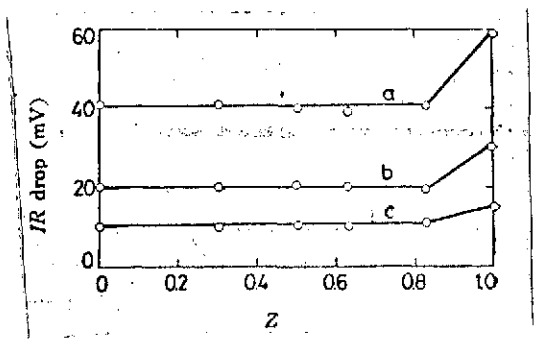

Fig. 9. IR drop in electrode
C/Pt (20μ$^{\phi}$), 3.0 mm thick, dissolved oxygen 200 cc/min/cm^2.
Current density (mA/cm^2)
a: 200; b: 100; c: 50

not change while the electrode thickness is 1.5-3.1 mm. When the thickness becomes larter than a certain size, the potential difference between the front and back side becomes larger also. When the current density is increased, the potential difference increases but its relation to the electrode thickness does not change. The hydrogen peroxide electrode should be as thin as possible due to the resistance from the decomposition materials. Even the dissolved oxygen electrode can be much thinner than the one we used here for the same effectiveness.

3.3. Analysis on IR drop and reaction distribution in the electrode

The results from the measurements of IR drop by the current interruptor method [8] are plotted in Fig. 9. The IR drop within the electrode is constant but that of the front side of the electrode is larger. As Ubrach [9] pointed out, it is very difficult to measure the polarization of the electrolyte within the porous electrode. The IR

drop in the electrode is attributed to the contact resistance of the electrode and capacitor and other measuring devices. The IR drop at the front part of the electrode is due to the resistance between the rough surface of the porous electrode and the capillary tips. /235

Let r = radius of porous electrode in cm.
l = length of porous electrode in cm.

Assume the electrode to be a cylinder in shape, then,
x = directional thickness of the electrode in cm.
z = x/l = the thickness of the electrode.
$I(mA/cm^2)$ = the current density within the electrode
$i(mA/cm^2)$ = the current density from electrochemical reaction within the electrode.
$E_1(mV)$ = the potential of the electrode
$E_2(mV)$ = the potential of the fluid
$\rho'(\Omega \cdot cm)$ = counterresistance of electrode
$\rho(\Omega \cdot cm)$ = counterresistance of electrolyte
$j(mA/cm^2)$ = electron current density of the electrode

Then,

$$dE_1/dz = \rho' l j \quad (1)$$

$$dE_2/dz = \rho l I \quad (2)$$

For the relation between the Faraday current and the current increment dI of the solution is

$$-2\pi r l i dz = \pi r^2 dI \therefore dI/dz = (-2l/r)i \quad (3)$$

If the situation where the change in the concentration of reactive material is small, then

$$i = (nFCD/\delta)\{1 - \exp(nF\eta/RT)\} \quad (4)$$

Here, $\eta = E_1 - E_2$, then

$$d\eta/dz = -\rho I + \rho' I_j, \quad \text{or } j + I = j_{z=0} (= \text{const.})$$
$$\therefore d\eta/dz = -(\rho + \rho') I + \rho' I_{z=0}$$

If the electrode is metal or carbon,[1]

$$d\eta/dz = -\rho I \tag{5}$$

Substituting Eqs. (3) and (4) into (5), we get

$$d^2\eta/dz^2 = (2\rho I^2/r)(nFCD/\delta) \{1 - \exp(nF\eta/RT)\} \tag{6}$$

Simplifying (6)

$$(d\eta/dz)^2 = (4\rho I^2/r)(nFCD/\delta) \int \{1 - \exp(nF\eta/RT)\} d\eta$$

Then, if z = l, $\eta = \eta_\ell$, $I = I_t$; z = 0 $|\eta| << |\eta_\ell|$, $|I| << |I_t|$, $d\eta/dz = 0$.

Then, Eq. (5) becomes

$$I_t = -2(nFCD/r\rho\delta)^{1/2} \{-\eta_l - (RT/nF) + (RT/nF)\exp(nF\eta_l/RT)\}^{1/2} \tag{7}$$

is negligible compared to η_ℓ, then,

$$I_t = -2(nFCD/r\rho\delta)^{1/2} \{-\eta_l - (RT/nF)\}^{1/2} \tag{8}$$

When $|\eta_l| \gg RT/nF$, the total current I_t is proportional to the square root of η_ℓ, where η_ℓ is the polarization of the frontal part of the electrode. Also, at the cathode $\eta < 0$, $I < 0$, $i < 0$.

Using Eq. (8), Fig. 4 was replotted as Fig. 10. It shows the relation between the square root of the polarization value and the current density and the necessity of the correlation by Eq. (6) when the polarization is minimal. From Eqs.(5) and (8)

$$d\eta/dz = k(-\eta - RT/nF)^{1/2} \tag{9}$$

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[1] $\rho/\rho' = 1000$ (ρ:1 N KOH)

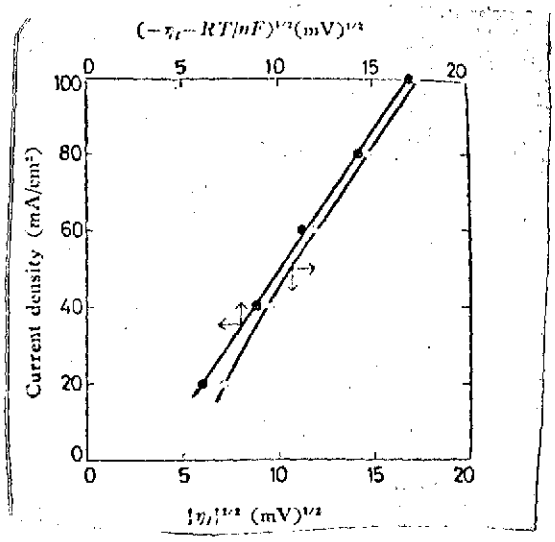

Fig. 10. The plots of $|I_t|-|\eta_\ell|^{1/2}$

C/Pt (20μ$^{\phi}$), 3.0 mm thick, dissolved oxygen 50 cc/min/cm^2

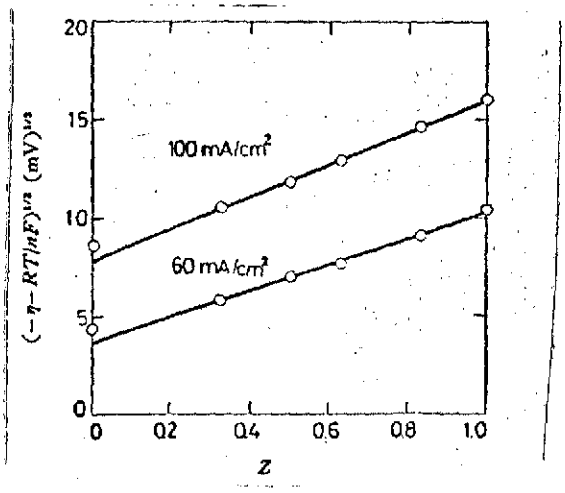

Fig. 11. The plots of $(-\eta - RT/nF)^{1/2} - z$

C/Pt (20μ$^{\phi}$), 3.0 mm thick, 50 cc/min/cm^2, dissolved oxygen electrode

Then,

$$z = k'\{(-\eta_z - RT/nF)^{1/2} - (-\eta_0 - RT/nF)^{1/2}\} \quad (10)$$

If we consider η_0 - $RT/nf^{1/2}$ negligible,

$$z = k'(-\eta_z - RT/nF)^{1/2} \quad (11)$$

Eq. 11 shows the potential distribution within the electrode. Using the above equation, Fig. 4 is replotted as Fig. 11. It shows that the potential distribution is related to the equation in a linear fashion. See Fig. 9. /236

4. Conclusion

1) The potential distribution in the porous carbon electrode with the cathode reaction of dissolved oxygen or hydrogen peroxide is influenced by the flow direction, especially in the case of hydrogen peroxide. On the basis of current usage and polarization, it is advantageous to apply the fluid from the front side of the electrode.

2. When hydrogen peroxide is used, the potential

distributes to the front of the electrode. Therefore, thin electrodes are recommended with hydrogen peroxide.

3. There is a linear relation between the square root of the polarization at the front side of the electrode and the total current.

4. There is also a linear relation between the square root of the polarization and the potential distribution within the electrode as a function of the direction and thickness of the electrode.

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